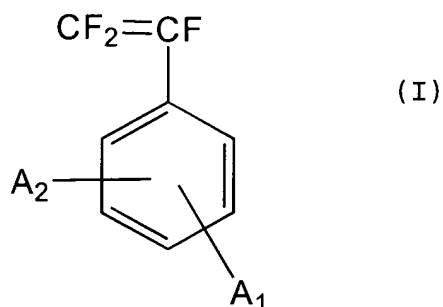
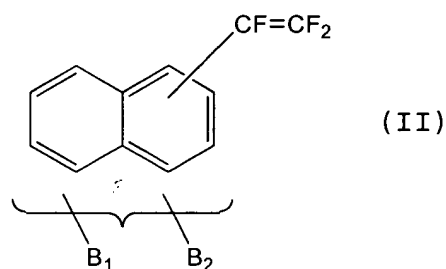


What is claimed is:

1. A membrane comprising a polymeric base film to which has been graft polymerized a monomer selected from the group consisting of monomers of formula (I)



15 and formula (II)



25 where A_1 , A_2 , and B_1 , B_2 are independently selected from the group consisting of:

hydrogen, lower alkyl, lower fluoroalkyl, cyclic alkyl, cyclic amine, cyclic ether, cyclic thioether,

aryl, provided that where one of A_1 and A_2 is hydrogen, aaryl is other than Ph, wherein Ph is phenyl,

5 CH(X)Ph, where X is selected from the group consisting of hydrogen, fluorine, lower alkyl, lower fluoroalkyl and Ph,

PRR' and P(OR)(OR'), where R and R' are independently selected from the group consisting of lower alkyl, cyclic alkyl and
10 Ph, and where R and R' can be the same or different, and

wherein A_1 , A_2 , B_1 , and B_2 can be the same or different, provided that in each monomer, at least one of the substituents A_1 ,
15 A_2 , B_1 , B_2 is other than hydrogen.

2. A membrane according to claim 1 comprising a polymeric base film to which has been graft polymerized a monomer of formula (I),
20 wherein A_1 is other than hydrogen, and A_2 is hydrogen.

3. A membrane according to claim 1 comprising a polymeric base film to which has been graft polymerized a monomer of formula (I),
25 wherein A_1 and A_2 are other than hydrogen.

4. A membrane according to claim 1 comprising a polymeric base film to which has

been graft polymerized a monomer of formula (II) wherein B_1 is other than hydrogen, and B_2 is hydrogen.

5 5. A membrane according to claim 1 comprising a polymeric base film to which has been graft polymerized a monomer of formula (II), wherein B_1 and B_2 are other than hydrogen.

10 6. A membrane according to claim 1 comprising a polymeric base film to which has been graft polymerized a monomer of formula (I) wherein A_1 is selected from the group consisting of lower alkyl and cyclic alkyl, and A_2 is the
15 same as A_1 or hydrogen.

 7. A membrane according to claim 1 comprising a polymeric base film to which has been graft polymerized a monomer of formula (II)
20 wherein B_1 is selected from the group consisting of lower alkyl and cyclic alkyl, and B_2 is the same as B_1 or hydrogen.

 8. A membrane according to claim 1
25 comprising a polymeric base film to which has been graft polymerized a monomer of formula (I) wherein A_1 is selected from the group consisting of cyclic amine, cyclic ether, cyclic thioether, and wherein A_2 is hydrogen.

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9. A membrane according to claim 1 comprising a polymeric base film to which has been graft polymerized a monomer of formula (I) wherein A_1 is selected from the group consisting
5 of aryl groups, and wherein A_2 is hydrogen.

10. A membrane according to claim 9, wherein said aryl group is a fused polycyclic aromatic with two fused rings.

11. A membrane according to claim 9, wherein said aryl group is biphenyl.

12. A membrane according to claim 9,
15 wherein said aryl group is a heteroaromatic group.

13. A membrane according to claim 12,
20 wherein said aryl group is a heteroaromatic group containing at least one heteroatom, wherein said at least one heteroatom is selected from the group consisting of nitrogen, oxygen and sulfur.

14. A membrane according to claim 13,
25 wherein said heteroaromatic group contains at least two of said heteroatoms, and said heteroatoms can be the same or different.

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15. A membrane according to claim 13,
wherein at least one of said heteroatoms is
nitrogen which is N-alkylated or N-benzylated.

5 16. A membrane according to claim 13,
wherein said heteroaromatic group is monocyclic.

10 17. A membrane according to claim 1
comprising a polymeric base film to which has
been graft polymerized a monomer of formula (I)
wherein A_1 is selected from the group consisting
of PRR' and $P(OR)(OR')$, where R and R' are
independently selected from the group consisting
of lower alkyl, cyclic alkyl and Ph, and where R
15 and R' can be the same or different, and wherein
 A_2 is hydrogen.

20 18. A membrane according to claim 1
comprising a polymeric base film to which has
been graft polymerized a monomer of formula (I)
wherein A_1 is selected from the group consisting
of Me and $CH(X)Ph$, where X is selected from the
group consisting of hydrogen, fluorine, Me, and
Ph, and A_2 is the same as A_1 or hydrogen.

25

19. A membrane according to claim 1
comprising a polymeric base film to which has
been graft polymerized a monomer of formula (II)
wherein B_1 is selected from the group consisting

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of Me and CH(X)Ph, where X is selected from the group consisting of hydrogen, fluorine, Me and Ph, and B₂ is hydrogen.

5 20. A membrane according to claim 1 comprising a polymeric base film to which has been graft polymerized a monomer of formula (I) wherein A₁ is Me and A₂ is Me or hydrogen.

10 21. A membrane according to claim 1 comprising a polymeric base film to which has been graft polymerized a monomer of formula (II) wherein B₁ is Me and B₂ is Me or hydrogen.

15 22. A membrane according to claim 1 comprising a polymeric base film to which has been graft polymerized a monomer of formula (I) wherein A₁ is para-Me, A₂ is hydrogen, and said base film comprises poly(ethylene-co-
20 tetrafluoroethylene).

 23. A membrane according to claim 1 comprising a polymeric base film to which has been graft polymerized a monomer of formula (II)
25 wherein B₁ is Me, B₂ is hydrogen, and said base film comprises poly(ethylene-co-tetrafluoroethylene).

 24. A membrane according to claim 1
30 comprising a polymeric base film to which has

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been graft polymerized one monomer selected from the group consisting of said monomers of formula (I) and formula (II), whereby the grafted chains are homopolymeric.

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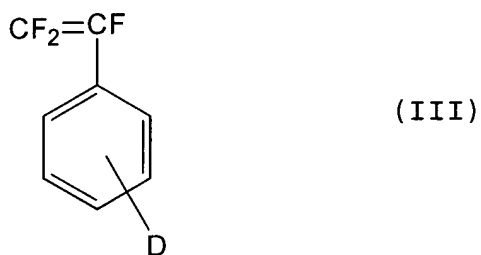
25. A membrane according to claim 1 comprising a polymeric base film to which has been graft polymerized more than one monomer selected from the group consisting of said
10 monomers of formula (I) and formula (II), whereby said grafted chains are copolymeric.

26. A membrane according to claim 1 comprising a polymeric base film to which has
15 been graft polymerized more than one monomer of formula (I), whereby the grafted chains are copolymeric.

27. A membrane according to claim 1
20 comprising a polymeric base film to which has been graft polymerized more than one monomer of formula (II), whereby the grafted chains are copolymeric.

28. A membrane according to claim 1
25 comprising a polymeric base film to which has been graft polymerized a monomer of formula (III) in addition to said monomers selected from the group consisting of monomers of formula (I) and
30 formula (II):

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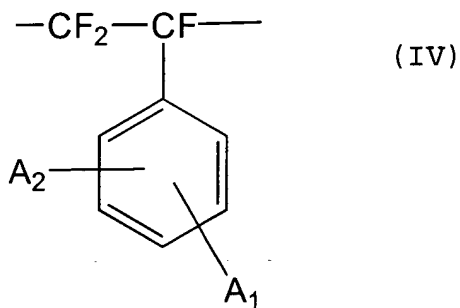
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where D is selected from the group consisting of hydrogen, fluorine, CF_3 , CF_2H , $\text{CF}=\text{CF}_2$, SO_2F and SO_3^-M^+ where M^+ is a suitable counterion.

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29. A membrane comprising a polymeric base film with grafted chains comprising monomer units selected from the group consisting of monomer units of formula (IV)

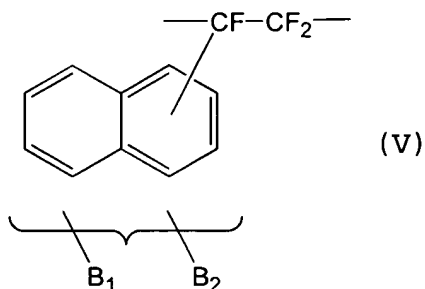
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20

and formula (V)

25



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where A_1 , A_2 , and B_1 , B_2 are independently
5 selected from the group consisting of:

hydrogen, lower alkyl, lower
fluoroalkyl, cyclic alkyl,
cyclic amine, cyclic ether, cyclic
thioether,

10 aryl provided that where one of A_1 and
 A_2 is hydrogen, aryl is other than Ph,

CH(X)Ph, where X is selected from the
group consisting of hydrogen, fluorine,
lower alkyl, lower fluoroalkyl and Ph,
15 wherein Ph is phenyl,

PRR' and P(OR)(OR') where R and R' are
independently selected from the group
consisting of lower alkyl, cyclic alkyl and
Ph, and where R and R' can be the same or
20 different,

and wherein A_1 , A_2 , B_1 , and B_2 can be the same
or different, provided that in each of said
monomer units at least one of the substituents A_1 ,
 A_2 , B_1 , B_2 is other than hydrogen.

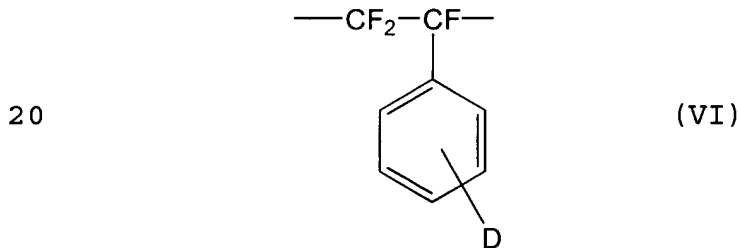
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30. A membrane according to any one of
claims 1, 20-23, 28 or 29 wherein at least a
portion of the grafted chains are crosslinked.

31. A membrane according to claim 29 wherein at least a portion of said monomer units further comprise at least one ion-exchange substituent, whereby said membrane is an ion-exchange membrane.

32. An ion-exchange membrane according to claim 31 wherein said at least one ion-exchange substituent is a sulfonate or sulfonic acid substituent.

33. An ion-exchange membrane according to claim 31 comprising a polymeric base film with grafted chains further comprising monomer units of formula (VI) in addition to said monomer units selected from the group consisting of monomer units of formula (IV) and formula (V):



where D is selected from the group consisting of hydrogen, fluorine, CF_3 , CF_2H , $\text{CF}=\text{CF}_2$, SO_2F and SO_3^-M^+ wherein M^+ is a suitable counterion.

34. An ion-exchange membrane according to claim 31 wherein at least a portion of said

monomer units comprise at least two ion-exchange substituents.

35. An ion-exchange membrane according to
5 claim 31 wherein at least 50% of said monomer units in said grafted chains have at least one ion-exchange substituent per monomer unit.

36. An ion-exchange membrane according to
10 claim 31 wherein said grafted chains comprise at least two different types of ion-exchange groups.

37. An ion-exchange membrane according to
15 claim 31 wherein said grafted chains comprise an anion-exchange group and a cation-exchange group.

38. An ion-exchange membrane according to
any one of claims 31 or 33 wherein at least a portion of the grafted chains are crosslinked.
20

39. An ion-exchange membrane according to
claim 31 wherein said ion-exchange membrane is substantially gas impermeable.

40. An ion-exchange membrane according to
25 claim 32 wherein said ion-exchange membrane is substantially gas impermeable.

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41. An ion-exchange membrane according to claim 31 wherein said monomer units are of formula (IV).

5 42. An ion-exchange membrane according to claim 41 wherein A_1 is selected from the group consisting of Me and $CH(X)Ph$, where X is selected from the group consisting of hydrogen, fluorine, Me and Ph, and A_2 is the same as A_1 or hydrogen

10

43. An ion-exchange membrane according to claim 41 wherein A_1 is Me and A_2 is Me or hydrogen.

15 44. An ion-exchange membrane according to claim 41 wherein A_1 is para-Me, A_2 is hydrogen, said base film comprises poly(ethylene-co-tetrafluoroethylene), and said at least one ion-exchange substituent is a sulfonate or sulfonic

20 acid group.

45. An ion-exchange membrane according to claim 31 wherein said monomer units are of formula (V).

25

46. An ion-exchange membrane according to claim 45 wherein B_1 is selected from the group consisting of Me and $CH(X)Ph$, where X is selected from the group consisting of hydrogen, fluorine, Me and Ph, and B_2 is hydrogen.

30

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47. An ion-exchange membrane according to claim 45 wherein B_1 is Me and B_2 is Me or hydrogen.

5

48. An ion-exchange membrane according to claim 45 wherein B_1 is Me, B_2 is hydrogen, said base film comprises poly(ethylene-co-tetrafluoroethylene), and said at least one ion-exchange substituent is a sulfonate or sulfonic acid group.

10

49. An electrode apparatus comprising an ion-exchange membrane of claim 39.

15

50. An electrode apparatus comprising an ion-exchange membrane of claim 40.

51. A membrane electrode assembly comprising an ion-exchange membrane of claim 39.

20

52. A membrane electrode assembly comprising an ion-exchange membrane of claim 40.

53. An electrochemical fuel cell comprising an ion-exchange membrane of claim 39.

25

54. An electrochemical fuel cell comprising an ion-exchange membrane of claim 40.

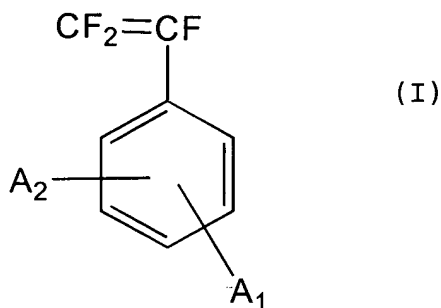
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55. An electrochemical fuel cell according to any one of claims 53 or 54 wherein said polymeric base film is less than 100 μm thick.

5 56. A membrane prepared by subjecting a membrane of claim 1 to a reaction process selected from the group consisting of halomethylation, sulfonation, phosphonation, amination, carboxylation, hydroxylation and
10 nitration.

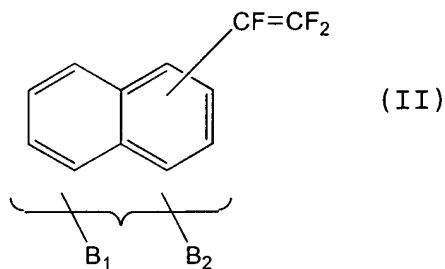
57. A method of preparing a membrane, said method comprising graft polymerizing to a polymeric base film a monomer selected from the
15 group consisting of monomers of formula (I)



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and formula (II)

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wherein in the selected monomer at
 10 least one of A_1 , A_2 , and at least one of B_1 , B_2 is
 a substituent other than hydrogen which activates
 said monomer with respect to said graft
 polymerizing, and said method further comprises:

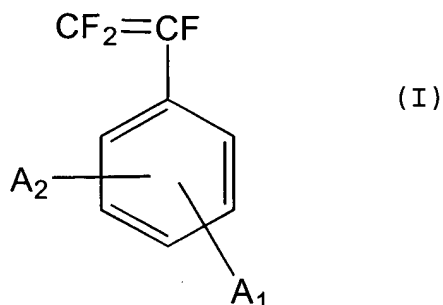
introducing a sulfonate group into at least
 15 a portion of said graft polymerized monomer
 units; and

converting at least a portion of said
 substituent to substituent which are deactivating
 with respect to desulfonation.

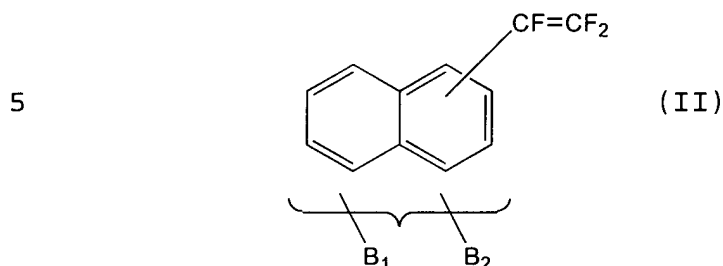
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58. A method of preparing a membrane, said
 method comprising graft polymerizing to a
 polymeric base film a monomer selected from the
 25 group consisting of monomers of formula (I)

30



and formula (II)



10 where A_1 , A_2 , and B_1 , B_2 are independently selected from the group consisting of:

hydrogen, lower alkyl, lower fluoroalkyl, cyclic alkyl, cyclic amine, cyclic ether, cyclic thioether,

15 aryl, provided that where one of A_1 and A_2 is hydrogen, aryl is other than Ph, wherein Ph is phenyl,

CH(X)Ph, where X is selected from the group consisting of hydrogen, fluorine, lower alkyl,
20 lower fluoroalkyl and Ph,

PRR' and P(OR)(OR') (where R and R' are independently selected from the group consisting of lower alkyl, cyclic alkyl and Ph, and where R and R' can be the same or different, and

25 wherein A_1 , A_2 , B_1 , and B_2 can be the same or different, provided that in each monomer at least one of the substituents A_1 , A_2 , B_1 , B_2 is other than hydrogen.

an aryl group selected from the group
5 consisting of monocyclic heteroaromatics, fused
polycyclic heteroaromatics, and heteroaromatic
ring assemblies having at least one nitrogen
atom,

10 phosphines of the formula PRR' and phosphites
of formula P(OR)(OR') where R and R' are
independently selected from the group consisting
of lower alkyl, cyclic alkyl and Ph, wherein Ph
in phenyl, and where R and R' can be the same or
15 different, and

60. A method according to claim 58, wherein A₁ and B₁ are independently selected from the group consisting of

phosphines of the formula PRR' and phosphites of formula P(OR)(OR') where R and R' are independently selected from the group consisting

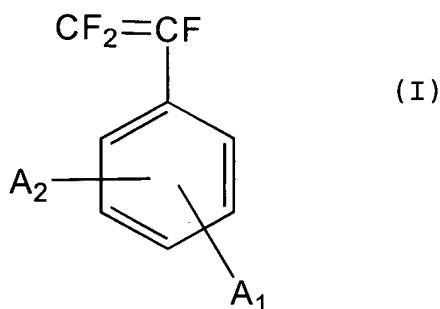
of lower alkyl, cyclic alkyl and Ph, and where R and R' can be the same or different, and

A₂ and B₂ are hydrogen,

the method comprising the sequential steps
5 of introducing a nitro group into at least a portion of the grafted monomer units of said membrane and converting at least a portion of said nitro groups to quaternary ammonium groups,

the method optionally further comprising
10 converting said phosphine or phosphite to an ion-exchange substituent.

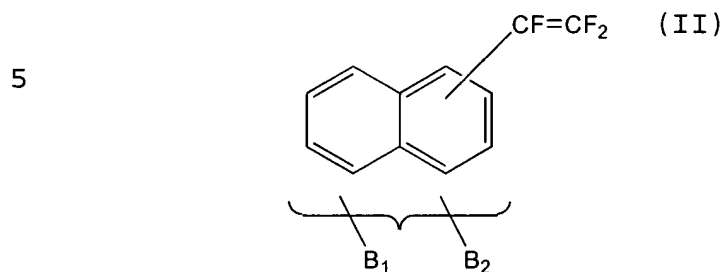
61. A method of preparing a membrane comprising graft polymerizing to a polymeric base
15 film a monomer selected from the group consisting of monomers of formula (I)



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25

and formula (II)



10

where A₁ and B₁ are independently selected from the group consisting of

PRR', P(OR)(OR'), and SR where R and R' are independently selected from the group consisting of lower alkyl, cyclic alkyl and Ph, and where R and R' can be the same or different, and

A₂ and B₂ are the same as A₁ and B₁ respectively or hydrogen,

20 the method further comprising oxidizing at least a portion of the PRR', P(OR)(OR'), or SR groups.

62. The method of claim 61 further comprising introducing ion-exchange substituents into at least a portion of said monomer units.

63. The method of claim 61, wherein A₁ and B₁ are independently selected from the group SR,

where R is selected from the group consisting of lower alkyl, cyclic alkyl and Ph, wherein Ph is phenyl, and A₂ and B₂ are the same as A₁ and B₁ respectively or hydrogen, and wherein the method
5 comprises converting at least a portion of the SR groups to sulfonate or sulfonic acid groups.

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